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PIGMENTS OF THE SPINEL TYPE

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Methods for the synthesis of cobalt-bearing spinel of different compositions are proposed. The use of such spinel in production of ceramic pigments makes it possible to eliminate a whole number of defects, in particular, the surface metallization defect in ceramics, and to ensure stable properties in the end product.

Pigments of the spinel type, which are characterized by the stability of their properties under the effect of various factors, are widely used in decorating ceramic articles [1 – 5]. The term "spinel" encompasses a large group of compounds with the common formula $A^{2+}B^{3+}O_4$, which have two cations in their composition: one cation with oxidation degree 2+ and the other cation with oxidation degree 3+ (A and B denote these cations) [6, 7].

The spinel structure is characterized by the distribution of cations between two types of vacancies: tetrahedral and octahedral. If cations A are arranged in octahedrons and have oxidation degree 2+, while cations B are in octahedrons and have oxidation degree 3+, such a spinel is called normal (ordinary). If cations B are located in tetrahedrons and cations A in octahedrons, such a spinel is called inverse. At the same time, cations B in the tetrahedral position preserve the oxidation degree 3+, and cations A in the octahedral position preserve the oxidation degree 2+. In this case, two cations with different oxidation degrees are found in the octahedral environment of the oxygen ion.

The inversion of spinel can be incomplete, and then the spinel is called partly inverse (mixed).

In most cases, elements A and B can have a different chemical nature. Depending on the nature of the prevailing cation in the octahedral position, spinels are classified as alumino-, ferro-, chromium-, titanium-vanadium spinels, etc.

The cation A^{2+} can be represented by various ions (Table 1) of bivalent metals: Zn, Mg, Cu, Fe, Mn, Ni, Co, Ba, Sr, and Cd; and cation B^{3+} by various ions of trivalent metals: Al, Fe, Mn, Cr, Zn, Ga, etc.

The distribution of cations in spinel is indicated in the following formulas:

normal $Me^{2+}_{[4]}Me^{3+}_{[4]}Me_{[6]}O_4$;

inverse $Me^{2+}_{[6]}Me^{3+}_{[6]}Me^{3+}_{[4]}O_4$;

partly inverse $Me^{2+}_{[1-x]}Me^{3+}_{[x]}Me^{3+}_{[2-x]}O_4$.

The sub-index in square brackets in the spinel formulas means the oxygen coordination number of the cation.

Owing to the difference in the values of ion stabilization energy in octahedral and tetrahedral positions, which were estimated and then empirically corroborated based on the analysis of absorption spectra of oxides and the results of determining magnetic sensitivity of magnet-diluted solid solutions, the physicochemical characteristics of spinels, especially their magnetic and electric parameters, perceptibly fluctuate depending on the composition and the arrangement of cations.

TABLE 1

Ions with oxidation degree 3+	Ions with oxidation degree 2+							
	Mg	Mn	Fe	Co	Ni	Cu	Zn	Cd
Al (aluminates)	N*	N	N	N	0.75	I**	N	N
V (vanadites)	N	N	N	–	–	–	–	–
Cr (chromites)	N	N	N	N	N	0.10	N	N
Mn (manganites)	–	N	–	–	–	–	N	–
Fe (ferrates)	0.90	N	I	I	I	0.86	N	N
Co (cobaltates)	–	–	–	N	–	–	–	–
Ga (gallites)	I	–	–	–	I	–	N	N

* N) Normal spinel.

** I) Inverse spinel.

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Main Physical Characteristics of Oxygen Spinels

Mohs hardness:	
normal spinel	7 – 8
inverse spinel	5 – 6
Density, g/cm^3	3.5 – 3.6
Melting point, °C	2030 – 2060
Cleavage	Absent or imperfect
Dielectric constant	8 – 9
Reactivity to solvents	Inert to acids and alkalis
Refractive index	1.72
Transmission in IR region	85% for monocrystal thickness 5 mm
TCLE at temperature 40°C, $10^{-6}\ °C^{-1}$	5.9
Magnetic properties	Para-, ferro-, and antiferromagnetic

It can be seen that spinels are high-melting and have high mechanical strength and chemical resistance. Thus, an equilibrium phase in the α-Al_2O_3 – α-Cr_2O_3 system is thermodynamically stable and forms a continuous series of solid solutions $Cr_xAl_{1-x}O_3$ at temperatures above 1200°C and $0.1 < x < 0.7$.

The affinity of structures and lattice parameters in many types of spinel determines one of its features: its capacity for the formation of solid substitution solutions (spinellides) between the spinels. Unlimited solubility, for instance, is established for crystals $MgAl_2O_4$ and $MgCr_2O_4$, $FeCrO_4$ and $FeFe_2O_4$, etc.

Complete isomorphic miscibility in spinels is observed for Mg^{2+} and Fe^{2+}; aluminum cation can be replaced by Fe^{3+} and Cr^{3+} with the formation of solid solutions between alumino- and ferrospinels, between alumino- and chromium spinels, etc. Some spinels form solid solutions with trivalent metal oxides, for example, $MgAl_2O_4$ with Al_2O_3, especially with the γ modification of Al_2O_3, whose crystalline lattice is close to the spinel lattice.

The solid solutions (Mg, Fe)(Al, Ti, Cr, Fe)$_2$O$_4$ are the most essential to ceramic technology, in particular, to the technology of spinel-type pigments. Furthermore, the following compounds are used in practice as ceramic pigments: $CaO \cdot Al_2O_3$, $MgO \cdot Cr_2O_3$, $FeO \cdot Cr_2O_3$, $MnO \cdot Al_2O_3$, $FeO \cdot Al_2O_3$, $ZnO \cdot Co_2O_3$, $MnO \cdot Co_2O_3$, $ZnO \cdot Cr_2O_3$, $ZnO \cdot Fe_2O_3$, $CuO \cdot Al_2O_3$, and others.

The formation of oxygen spinels proceeds at high temperatures up to 1750 – 1850°C. To lower the pigment synthesis temperature, boric acid is used as a mineralizing agent, which makes it possible to bring this temperature down to 1300 – 1350°C.

It is known that the introduction of a mineralizing agent to the composition of the initial mixture decreases the melt viscosity and the sintering temperature of a ceramic material. The choice of the mineralizer composition is based on the analysis of phase diagrams of different systems, in this case, the systems containing B_2O_3 [6 – 8]. Thus, a wide region of non-miscible liquids was identified in the B_2O_3 – MgO – SiO_2 ternary system. The fields of cristobalite, protoenstatite, and magnesium perborate are overlapped by the region of non-miscible melts (Table 2).

No ternary compounds were found in the Al_2O_3 – B_2O_3 – SiO_2 system. It is assumed that a continuous region of solid solutions probably exists between the binary compounds $3Al_2O_3 \cdot 2SiO_2$ and $9Al_2O_3 \cdot 2B_2O_3$. In the Na_2O – B_2O_3 – SiO_2 system, it was mostly the region with an Na_2O content below 50% that was investigated. The existence of one ternary compound $Na_2O \cdot B_2O_3 \cdot 2SiO_2$ melting at a temperature of 766°C (similarly to danburite $CaO \cdot B_2O_3 \cdot 2SiO_2$) was identified in this system. The invariant points of the Na_2O – B_2O_3 – SiO_2 system are shown in Table 3.

As can be seen, the introduction of boric acid into a spinel composition produces a significant decrease in the temperature of its synthesis. Considering the multicomponent composition of the initial mixture, one can state that after its high-temperature treatment, a material with a complex phase composition is formed.

The spinel-based pigments were first synthesized by Prof. S. G. Tumanov [3]. He obtained excellent ceramic pigments based on cobalt and nickel spinels, which have high thermal resistance.

Table 4 indicates the properties of spinels, which can be used to synthesize various pigments.

TABLE 2

Phase	State of system	Composition, wt.%			Temperature, °C
		MgO	B_2O_3	SiO_2	
At equilibrium with one liquid					
$MgO + 3MgO \cdot B_2O_3 + 2MgO \cdot SiO_2$	Eutectic	64.0	31.0	5.0	1327 ± 10
$3MgO \cdot B_2O_3 + 2MgO \cdot B_2O_3 + 2MgO \cdot SiO_2$	The same	56.7	37.3	6.0	1270 ± 5
$2MgO \cdot B_2O_3 + 2MgO \cdot SiO_2 + MgO \cdot SiO_2$	Peritectic	42.4	30.6	27.0	1203 ± 5
$MgO \cdot SiO_2 + SiO_2$	Monotectic	37.0	8.0	55.0	1510 ± 20
$2MgO \cdot B_2O_3 + MgO \cdot SiO_2$	The same	1.0	10.0	89.0	1186 ± 5
$2MgO \cdot B_2O_3$	–	38.0	37.0	25.0	1200 ± 5
At equilibrium with one liquid in the temperature maximum points					
$2MgO \cdot SiO_2 + 3MgO \cdot B_2O_3$ + liquid	–	63.0	32.0	5.0	1331 ± 5
$2MgO \cdot SiO_2 + 2MgO \cdot B_2O_3$ + liquid	–	54.0	36.0	10.0	1283 ± 5

TABLE 3

Phase	State of system	Composition, wt.%			Tempera-ture, °C
		Na_2O	B_2O_3	SiO_2	
Double invariant points					
$Na_2O \cdot B_2O_3 + Na_2O \cdot 2B_2O_3$ + liquid	Eutectic	32	68	–	1073
$Na_2O \cdot 2B_2O_3 + Na_2O \cdot 4B_2O_3$ + liquid	The same	28	72	–	995
$Na_2O \cdot 3B_2O_3 + Na_2O \cdot 4B_2O_3$ + liquid	Peritectic	24	76	–	1039
$Na_2O \cdot B_2O_3 + Na_2O \cdot B_2O_3$ + liquid	Eutectic	49	24	27	1106
$Na_2O \cdot B_2O_3 + SiO_2$ + liquid	The same	27	41	42	803
$Na_2O \cdot 4SiO_2 + SiO_2$ + liquid	″	12	55	33	948
Triple invariant points					
$Na_2O \cdot B_2O_3 + Na_2O \cdot 2SiO_2 + Na_2O \cdot SiO_2$ + liquid	Peritectic	33	18	49	913
$Na_2O \cdot B_2O_3 + Na_2O \cdot 2SiO_2 + SiO_2$ + liquid	Eutectic	27	25	48	793
$Na_2O \cdot B_2O_3 + Na_2O \cdot 2B_2O_3 + SiO_2$ + liquid	The same	33	18	49	913
$Na_2O \cdot 3B_2O_3 + Na_2O \cdot 4B_2O_3 + SiO_2$ + liquid	Peritectic	33	18	49	913
$Na_2O \cdot B_2O_3 \cdot SiO_2 + Na_2O \cdot B_2O_3 + Na_2O \cdot 2B_2O_3$ + liquid	Eutectic	32	68	—	1013

The main raw material for the synthesis of spinel-type pigment is technical alumina, which is subjected to heat treatment at 1300°C and subsequent washing for the purpose of removing sulfates. The synthesis of pigments is carried out at 1300°C in a weakly oxidized medium with 0.5-h exposure, and boric acid in the amount of 2% of the total mixture weight is used as a mineralizer.

The most intense tint is accomplished in pigments synthesized from oxides after thorough mixing, with boric acid additive, or obtained through mixing the respective crystalline salts or metal hydroxides precipitated with ammonium solution. When the initial components are salts and metal hydroxides, the firing temperature of the pigment significantly decreases.

Table 5 shows the compositions and color characteristics of several light-blue cobalt-bearing pigments of the spinel type, which were produced with boric acid as mineralizer (2% of the mixture weight) [3].

With an excessive content of aluminum oxide, the latter is released in the form of corundum. The refractive index of the spinel-type pigments increases with increasing content of cobalt oxide.

TABLE 4

Chemical formula	Crystalline syngony	Density, kg/m^3	Melting point, °C	TCLE, 10^{-5}, °C^{-1}
$CuAl_2O_4$	Cubic	4.58	Incongruent	–
$MgAl_2O_4$	The same	3.58	2135	0.543
$CuAl_2O_4$	Rhombic	3.67	1600	0.680
$SrAl_2O_4$	Tetragonal	–	2015	–
$BaAl_2O_4$	Hexagonal	–	1820	–
$ZnAl_2O_4$	Cubic	4.58	1930	0.596
$MnAl_2O_4$	The same	4.12	1930	–
$FeAl_2O_4$	The same	4.39	1780	0.900
$FeAl_2O_4$	The same	4.37	1960	–
$CoAl_2O_4$	Tetragonal	4.45	2020	–
$ZnMn_2O_4$	The same	4.70	1700	–
MgV_2O_4	Cubic	4.85	1560	–
$MgLa_2O_4$	The same	4.57	1560	–

It can be seen from the data in Table 5 that the most intense color is registered in pigments 2a, 38, and 39, in which the limiting ratio of aluminum oxide : cobalt oxide is equal to 1 : 3. However, as the aluminum oxide content increases, the share of the green color becomes greater, in particular, a green-colored compound $7CoO \cdot 5Al_2O_3$ was registered.

Blue spinel-type pigments were synthesized in the $CoO – Al_2O_3 – SiO_2$ system [4]. With an increasing silica content, the pigment color varies from turquoise (5% SiO_2) to dark blue (17% SiO_2).

Based on magnesia spinel, pigments were obtained in the $CoO – MgO – Al_2O_3$ system by substituting chromium oxide for aluminum oxide.

The composition of the pigment with the optimum properties correlates with the formula $0.5CoO \cdot 0.5MgO \cdot 0.1Al_2O_3$. A boric acid additive substantially increases the yield of the formed spinel and improves the pigment color intensity and its acid resistance.

The pigments in the $CoO – ZnO – Al_2O_3$ system can be regarded as typical spinel tinted in an intense blue color. The

TABLE 5

Pigment	Al_2O_3 content,* mole	Photometric chromaticity, %		
		red	green	blue
1	1.0	15.24	16.88	67.88
1a	1.0	21.00	23.00	54.00
2	2.0	12.00	13.00	73.24
2a	2.0	13.00	10.00	75.00
38	3.0	10.00	12.00	76.00
39	4.0	11.00	13.00	74.00
40	5.0	11.00	13.00	75.30
41	8.0	14.00	18.00	66.00
42	10.0	15.00	18.00	66.00
14	20.0	21.00	19.00	59.00
136	100.0	29.00	28.00	41.00
137	200.0	29.00	29.00	40.00

* All pigments contain 1.0 mole of CoO.

color brightness in such pigments perceptibly increases as the firing temperatures grows (1350°C) and boric acid is introduced. Already at temperature of 900 – 1000°C, sky-blue pigment tinting is visible, which little varies at higher firing temperatures, even at 1300°C.

The study of the effect of aggressive reactants on the chemical resistance of pigments revealed that the highest resistance to the dissolving effect of acids is observed in the pigment of the zinc series. As for the individual components of porcelain glaze and ceramic mixture, the most perceptible destruction of pigments is produced by chalk, magnesite, and partly quartz, especially the destruction of the magnesia series of pigments.

The x-ray study identified the presence of spinel in the pigments of the $Al_2O_3 – Cr_2O_3$ system [2], which were synthesized from potash alum calcined at a temperature of 1300°C. These pigments had the following composition (wt.%) [4]: 50.0 – 95.5 Al_2O_3, 0.5 – 50.0 Cr_2O_3, and 5.0 H_3BO_3 (above 100%).

The pigments synthesized in the $Al_2O_3 – Cr_2O_3$ system represent tinted corundum, whose light absorption curves are similar to those of natural rubies. As the Cr_2O_3 content in the pigment composition increases, its refractive index does not vary. The introduction of a mineralizing additive (boric acid) increases the refractive index and the color intensity of the pigment. The resistance of the pigments when used as underglazes and overglazes becomes higher.

Tumanov [3] replaced aluminum oxide with chromium oxide in magnesia spinel of the $MgO – Al_2O_3$ system. The initial components were magnesium and aluminum oxides, which were obtained from ammonium alum previously calcined at 1300°C and thoroughly washed.

The firing of the pigment was carried out at 1300°C in an oxidizing medium; the exposure was 0.5 h. The mineralizers were boric acid and sodium and potassium carbonates. The following composition of the pink pigment based on magnesia spinel is recommended (wt.%): 8.44 – 20.32 MgO, 0.12 – 12.00 Cr_2O_3, 8.06 Al_2O_3 (constant), 1.42 H_3BO_3, 1.42 Na_2CO_3, and 1.42 K_2CO_3. With the Cr_2O_3 content in this pigment equal to 7%, the share of the red color in the color characteristics amounted to 40.8%. As the Cr_2O_3 content in the mixture increases to 50%, the share of red color gradually decreases to 37.4%.

The phase composition of this pigment exhibited corundum, along with spinel. As a consequence of preliminary calcination of alumina accompanied by the transformation $\gamma\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$, approximately 30% spinel is formed, whereas the remaining part is made of corundum and periclase.

Heat-resistant pigments of the spinel type were synthesized in the $MnO – Al_2O_3 – Cr_2O_3$ system [4], which are recommended for use in underglaze and overglaze ceramic paints. These pigments have high thermal and chemical resistance.

TABLE 6

Paint number	Composition of blue paint mixtures (wt.%)*					
	cobalt(II) oxide	dolomite	kaolin	quartz	feldspar	crushed porcelain
28	30.00	9.00	3.00	12.00	28.00	18.00
29	30.00	9.00	1.91	–	41.00	18.00
30	50.00	5.38	1.91	17.17	14.67	10.77
31	50.00	5.38	1.91	10.54	21.40	10.77
32	25.00	–	–	25.00	–	–
33	7.50	–	–	22.50	21.00	23.50

* Paint 32 additionally contained 50.0% porcelain glaze mixture, and paint 33 additionally contained 25.50% alabaster.

Furthermore, spinel-type pigment compositions of bright color tones have been developed on the basis of oxides of bivalent and trivalent metals and can be used as overglaze paints. Such pigments are aluminates, chromites, or ferrites, resistant to the dissolving effect of glaze melt and flux. The spinel-type pigments have the following colors: $NiO – Al_2O_3$ — dark blue; $CoO – Cr_2O_3$ — dark green; $MnO – Cr_2O_5$ — greenish-gray; $MgO – Fe_2O_3$ — yellowish-gray.

Spinel can be produced by evaporation of a mixture of equivalent quantities of metal nitrates and subsequent calcination of the precipitate at a temperature of 900 – 1000°C, or by coprecipitation of metal hydroxides with subsequent calcination of the obtained precipitate. Thus, the equimolar substitution of Co^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, and Cd^{2+} for Mg^{2+} and Zn^{2+}, as well as substitution of Cr^{3+} and Fe^{3+} for Al^{3+} in chromite $MgCr_2O_4$ led to the synthesis of spinel-type pigments, whose color varied from pink to blue tones.

By replacing Zn^{2+} in willemite Zn_2SiO_4 with two-charge ions of transition metals, and replacing Si^{4+} ions with Sn^{4+}, Zr^{4+}, and Ti^{4+}, a group of sky-blue and blue pigments was developed, which were successfully used in decorating porcelain articles. However, cobalt compounds became the most common in production of intense blue pigments. The oxide of this chemical element is used for ceramic mixture tinting, as well as in the compositions of blue and light-blue overglaze and underglaze ceramic paints of various tones. Among the numerous modifications of cobalt oxide described in the literature, the existence of only three of them is certain: CoO, Co_3O_4, and Co_2O_3. It was found that the lower cobalt oxide is transformed into higher oxides: Co_3O_4 and Co_2O_3. Under elevated temperatures, these oxides dissociate into oxygen and a lower cobalt oxide. Cobalt oxide as a technical material always contains small quantities of other metal impurities (nickel, manganese, and iron). The compositions of ceramic paint mixtures produced at the Dulevo Paint Works, which contain cobalt oxide, are given in Table 6.

The compounds of Co(II) used as pigments have blue, bluish-yellow, green, and violet colors. They are represented by four types of compounds:

– spinels of the composition AX_2O_4 or A_2ZO_4, where A is Co, partly with Zn and Mg impurity, X is Al, Fe, Cr, V, Mo, or W, and Z is Sn, Ti, or Zr;

– mixed oxides $CoO_x \cdot MeO$;

– mixed cobalt-zinc silicates of the willemite structure $CoO_x \cdot ZnO_y \cdot SiO_2$;

– simple cobalt salts: phosphates and arsenates.

The cobalt-bearing pigments of all four types are resistant to alkalis and high temperatures and have high light and atmospheric resistance. However, the majority of light-blue pigments are produced on the basis of cobalt aluminate $CoAl_2O_3$ of an intense blue color. It is formed in firing at 1100°C from an equimolar mixture of cobalt and aluminum nitrates. Firing of the initial mixture is carried out in an oxidizing gas medium with a strictly controlled exposure at the final temperature. Light-blue pigments can also be formed as a consequence of reactions between cobalt oxide and silicon oxide. In this case, the pigment color varies from dark blue and bright blue to sky-blue, depending on the quantity of cobalt oxide. The pigment color to a great degree is determined by the presence of particles of a certain microscopic size, which, under the preset firing conditions, are insoluble in the melt, transforming into the vitreous phase in cooling. The rate of the dissolution of pigment particles in the melt depends on their initial size, firing temperature, and duration of exposure at the maximum temperature, as well as on the melt and the pigment compositions. With the aim of improving the color characteristics and increasing the stability of properties, the synthesis of blue and light-blue pigments was implemented in various systems.

One of the main systems used in selecting spinel-type pigment compositions was $MgO – Al_2O_3 – SiO_2$. Apart from binary magnesium silicates $2MgO \cdot SiO_2$, $MgO \cdot SiO_2$ and aluminum silicate $3Al_2O_3 \cdot 2SiO_2$, another binary oxide exists in this system, namely, magnesia or noble spinel $MgO \cdot Al_2O_3$, which congruently melts at 2135°C. It is precisely spinel that is the primary product of solid-phase reactions in the $MgO – Al_2O_3 – SiO_2$ system with variable ratios of initial oxides, since spinel has the highest rate of formation. In addition, there are ternary oxides in this system, which are represented by cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ and sapphirine $4MgO \cdot 5Al_2O_3 \cdot 2SiO_2$, as well as cordierite-like phases forming solid solutions.

However, in the synthesis of spinel-type pigments, one should take into account the data indicating that the noble spinel crystals have the highest rate of the formation in this system. It should also be noted that the relatively low temperature of porcelain firing accepted at most Russian factories (not more than 1320°C) prevents accomplishing sufficient color brightness in ceramic paints based on spinel-type pigments. At the same time, at higher temperatures, cobalt-bearing pigments manifest an instability of properties, which is determined by the capacity of cobalt oxide for dissassociation at high temperatures.

In this connection, special methods are proposed for the synthesis of cobalt-containing spinel of various compositions, whose application in ceramic paint production makes it possible to exclude a whole series of defects, in particular, the metallization of the ceramic article surface, and to ensure the stability of properties in the end product. Thus, to produce blue underglaze, it is recommended [9] to use spinel of the composition $Mg_{1-n}Co_nAl_2O_4$ (n = 0.32, 05, 0.7, 0.9) obtained by precipitation from aqueous solutions of the respective nitrates in the presence of NH_4OH, washing of the precipitate, its drying, and subsequent firing at temperatures above 500°C.

As the firing temperature increases, the spinel phase content in the spinel of composition $Mg_{0.1}Co_{0.9}Al_2O_4$ grows, and its complete crystallization is accomplished at 1000°C with the formation of a new phase with the composition $MgAl_2O_4$.

With increasing temperature, the share of pigment particles sized 4 – 7 μm grows from 32 to 42%. The share of fine-dispersion particles of size 2 – 4 μm decreases from 37 to 24%. It was experimentally found that the optimum particle size for spinel used in ceramic paint production, to ensure high-quality decorating, should be 4 – 9 μm.

Furthermore, to produce high-quality paints based on cobalt-containing spinels, one should take into account several technological parameters, namely, the paint-layer thickness, the compliance of the initial component quality with the standard requirements, the use of dextrin, which has special properties, in the paint production, etc.

Strict adherence to the technological regimes makes it possible to exclude the formation of defects in decorating ceramics articles and to ensure a high quality of decorative spinel coatings for ceramics.

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